10/586282
IAP11 Rec'd PCT/PTO 18 JUL 2006

DOPED LiF MONOCHROMATOR FOR X-RAY ANALYSIS

The invention relates to a lithium fluoride doped with a divalent positive ion, to a single crystal of said fluoride and to the use of said single crystal as an X-ray monochromator, especially in X-ray fluorescence analysis machines, in X-ray diffraction machines, in electron microprobes and in transmission microscopes. All these analytical techniques employ a monochromator crystal. This crystal receives the X-radiation that it is desired to analyze and separates the various components (or wavelengths) that it contains by diffraction according to Bragg's law and these components leave the crystal at specific angles. This separation results in a set of diffraction lines. A detector placed in the path of the line at a suitable angle determined by Bragg's law converts the X-radiation into an electrical signal.

Within the context of the present invention, the X-radiation is understood to mean an electromagnetic wave having an energy between 0.1 and 1 000 keV, more particularly between 1 and 100 keV.

In the aforementioned analytical machines, the X-radiation may be of various origins. To take an example, the elemental analysis of a specimen by X-ray fluorescence is a nondestructive method based on the detection and analysis of the X-rays that are emitted by said specimen and are then collected by a monochromator crystal that diffracts said X-rays according to Bragg's law.

According to that method, the specimen is irradiated by a beam of high-energy X-rays (in the case of an X-ray fluorescence spectrometer) or by a beam of electrons (in the case of a microprobe that may, for example, be incorporated into a scanning electron microscope). This primary beam excites the specimen, which then emits a

secondary beam of X-rays, also called X-ray fluorescence. This X-ray fluorescence secondary radiation contains wavelengths characteristic of the chemical elements contained in the specimen. The monochromator crystal separates the various components that it contains by diffraction and they leave the crystal at specific angles. This separation results in a set of diffraction lines. A detector placed in the path of the line at a suitable angle (according to Bragg's law) converts the X-ray fluorescence radiation into an electrical signal. Specific intensities may be accumulated for each X-ray fluorescence line characteristic of a chemical element contained in the specimen. The chemical concentrations of various elements may thus be determined by reference to a prior calibration.

A high X-ray sensitivity is expected of such an analytical system, resulting, in the case of X-ray fluorescence, in a high detectability with the best possible precision for detecting very small quantities of an element. The sensitivity is higher the more intense the X-radiation reaching the detector. In the case of X-ray fluorescence, this intensity depends, of course, on the specimen itself, on the targeted chemical element and on the chosen fluorescence line, but also on the monochromator and on the detector. This is because the monochromator may reflect the X-radiation to a greater or lesser extent.

Whatever the type of analysis, the aim is to have monochromators that reflect as much as possible, in order to lose the least possible amount of intensity during the diffraction step.

The quality of the detector is also important, as there is no point using a highly reflective monochromator sending very intense radiation back to the detector if the latter is capable of measuring it. The detector

generally comprises a scintillator and a photoreceiver. The scintillator converts the X-ray energy lost on ionizing into light pulses. The light pulses are received by a photoreceiver, which converts them into an electrical signal. The photoreceiver is usually a photomultiplier tube (or PMT) or a photodiode or other device. The X-radiation striking the scintillator is saturated above a certain intensity (i.e. after a certain number of counts received for a given period of time). This is because, after each X-ray detection (that is to say each time a pulse is counted), the scintillator has a decay time over which any other detection is impossible. A common scintillator such as thallium-doped sodium iodide (Tl:NaI) has a decay time of about 230 ns. This time is determined by fitting a sum-of-exponentials (or integral-of-exponentials) law to the scintillator signal as a function of time. By convention and throughout the rest of the text, only the decay time will be relative to the predominant light component given. With such a scintillator, the maximum counting rate is about 4 million interactions per second. In practice, this value is generally reduced by a factor of 2. In many cases, owing to long decay time of the scintillator, a filter has to attenuate the intensity of the X-radiation.

According to the invention, it has been discovered, firstly, that a single crystal of LiF doped with a divalent positive ion, used as monochromator, has a high reflectivity and, secondly, that the strong radiation emanating from the monochromator can be effectively received by a fast light scintillator, for example of the rare-earth halide type.

The lithium fluoride used in the context of the invention contains at least 0.014 mol and preferably at least 0.018 mol per kg of a divalent positive ion M present in the fluoride state. The ion M is present in fluoride form, that is to say MF_2, in the lithium

fluoride LiF. The M contents are given in mols of M (and not in mols of MF_2) per total weight in kilograms of doped fluoride, that is to say per kilogram of fluoride containing Li and M (and not pure LiF). Preferably, the atomic number of M is from 10 to 35. Preferably, the ionic radius of divalent M varies from 55 to 80 picometers. The ion M is such that MF_2 exists. The ion M may especially be Mg^{+}, Co^{2+} or Zn^{2+}. The ion M may also be a mixture of at least two ions chosen from Mg^{2+}, Zn^{2+} and Co^{2+}. The ion M is preferably Mg^{2+}. The table below gives a few characteristics of these ions.

	Mg^{2+}	Co^{2+}	Zn^{2+}
Atomic number	12	27	30
Ionic radius (in picometers)	65	72	74

The following table gives the equivalences between M contents expressed in mol/kg and Mg^{2+}, Co^{2+} or Zn^{2+} contents expressed in ppm by weight.

M (mol/kg)	Mg^{2+} (ppm by weight)	Co^{2+} (ppm by weight)	Zn^{2+} (ppm by weight)
0.018	438	1060	1177
0.020	486	1179	1308
0.023	559	1355	1504
0.025	608	1473	1635
0.045	1094	2652	2942
0.082	1993	4832	5361

The concentrations of M may be analyzed by ICP spectroscopy (induction-coupled plasma spectroscopy). Preferably, the fluoride contains at least 0.02 mol and even at least 0.023 mol and even at least 0.025 mol of M per kg of fluoride.

The fluoride generally contains at most 0.082 mol and even more generally at most 0.045 mol of M per kg of

fluoride.

If the fluoride according to the invention contains too much M (more than 0.045 mol of M per kg), the single crystal may become brittle and cracks may be observed.

The LiF may be manufactured in the single-crystal state from pure LiF and pure MF_2 (for example MgF_2, CoF_2 or ZnF_2) powders. The powders are placed in a crucible compatible with its contents, generally a platinum or graphite crucible. The whole assembly is then heated until the powders melt, generally at between 800 and 1 000°C, more particularly to above the melting point of LiF, which is about 870°C, the materials then undergoing congruent crystallization resulting in a single crystal or a few large single crystals. The crystallization technique may be the Czochralski, Kyropoulos or Bridgeman-Stockbarger method. The latter technique generally results in a polycrystal containing large single crystals (single-crystal volume of the order of 1 to 10 cm^3). The Czochralski method and the Kyropoulos method lead to single crystals and involve a seed. The seed may be pure LiF or LiF doped with M.

The material obtained by these growth methods is then used to obtain single crystals generally having the form of a cube or parallelepiped, the thickness of which varies from 0.05 mm to 10 mm in thickness and the two main parallel surfaces of which (one being intended to receive and reflect the X-radiation) have an area ranging from 0.5 to 30 cm^2. These single-crystal components may be made from the material coming directly from the growth, for example by cleaving (essentially along the (200) crystal plane).

When the material is used in a sequential spectrometer, a parallelepiped with a thickness ranging from 1 to 10 mm is generally prepared, the surface of which may be obtained by cleaving or more generally by mechanical

erosion with an abrasive or by chemical-mechanical erosion.

When the material is used in a simultaneous spectrometer, then parallelepipedal, and generally cleaved, thin plates ranging in thickness from 0.05 to 1 mm are generally prepared, on which in general a concave shape is imposed by application to a concave support. In this case, the monochromator also has a focusing action. Thus, within the context of the invention, individual single crystals (not agglomerated with another single crystal), the volume of which ranges from 2.5×10^{-3} cm^3 to 30 cm^3 and more generally from 0.01 to 20 cm^3, are prepared and used.

It has been observed that the intensity reflected by the M:LiF single crystal according to the invention (especially when M is Mg) increases very substantially when the wavelength of the reflected line decreases, especially for wavelengths below 3 Å, and even below 2 Å and even below 1.5 Å.

The invention also relates to a method of analysis for an element using an analytical machine that includes a monochromator made of the fluoride according to the invention and to a scintillator coupled to said monochromator, said scintillator being locked onto a line of wavelength below 3 Å, or below 2 Å, or below 1.5 Å.

The increase in intensity reflected by the M:LiF single crystal according to the invention is particularly spectacular when the M content increases, in particular at short wavelengths. This wavelength effect is more particularly observed for a cleaved surface finish. For a surface finish prepared by mechanical erosion (for example using an abrasive such as silicon carbide, boron carbide or diamond) or even by chemical-mechanical erosion, an increase in the intensity

reflected by the M:LiF single crystal according to the invention is also observed (but this is less spectacular than in the case of the cleaved surface) in particular at short wavelengths.

The increase in intensity (for the (200) crystal plane) is maintained after the plane single-crystal plates have been curved, especially in the case of a cleaved surface finish.

Without the Applicant being held to any theoretical consideration, the X-ray reflectivity properties could be attributed to insertions or substitutions of M (as Mg^{2+}) in the cation lattice. The invention therefore relates to LiF doped with at least one divalent ion M such as Mg^{2+} having an ionic radius close to that of Li^{+} (60 picometers), in particular Mg^{2+}, Co^{2+} and Zn^{2+}. These ions offer the advantage of an atomic number that is still low (therefore providing a lower X-ray absorption) and have, in the form of fluorides (especially MgF_2, CoF_2 and ZnF_2), physical properties that are compatible with the melting of LiF (melting points: 1 200°C and 872°C, respectively; boiling points: 1 400°C and 1 500°C, respectively).

The invention also relates to the combination of the M:LiF single crystal according to the invention as monochromator with a detector comprising a fast scintillator (delay time less than 30 ns on its principal component) and allowing counts of at least 10 million per second to be achieved. It is also preferable to use a scintillator exhibiting good resolution of its energy spectrum. The energy resolution ($\Delta E/E$) is usually determined, for a given detector and for a given incident energy, as the half-height width of the peak in question in an energy spectrum obtained from this detector, with respect to the energy of the centroid of the peak (see especially: G.F. Knoll "*Radiation detection and measurement*", John

Wiley & Sons, Inc., 2nd edition, page 114). This combination according to the invention increases the number of X-ray fluorescence photons analyzed. The analysis statistics are therefore improved. The result, in the case of the analytical machine, is better analytical quality and a reduction in measurement time.

As suitable scintillator, it is possible to use a polycrystalline or single-crystal material containing a rare-earth halide. These crystals have the advantage of having both a short decay time (for example 28 ns in the case of $La_{0.9}Ce_{0.1}Cl_3$, a figure obtained by fitting to a simple exponential model) and good energy resolution (3.9% with ^{137}Cs). As rare-earth halides more particularly concerned, mention may especially be made of:

- ALn_2X_7 in which Ln represents one or more rare earths, X represents one or more halogen atoms, chosen from Cl, Br or 1, and A represents an alkali metal such as Rb and Cs;
- $LaCl_3$, which may in particular be doped with 0.1 to 50 wt% $CeCl_3$;
- $LnBr_3$, which may in particular be doped with 0.1 to 50 wt% $CeBr_3$;
- $LaBr_3$, which may in particular be doped with 0.1 to 50 wt% $CeBr_3$;
- $GdBr_3$, which may in particular be doped with 0.1 to 50 wt% $CeBr_3$;
- $La_xLn_{(1-x)}X_3$, which may in particular be doped with 0.1 to 50% CeX_3, where x may range from 0 to 1, Ln being a rare earth different from La, and X being a halogen as mentioned above;
- $La_xGd_{(1-x)}Br_3$, which may in particular be doped with 0.1 to 50 wt% $CeBr_3$, it being possible for x to range from 0 to 1;
- $La_xLu_{(1-x)}Br_3$, which may in particular be doped with 0.1 to 50 wt% $CeBr_3$, it being possible for X to range from 0 to 1;
- $Ln'_xLn''_{(1-x)}X'_{3(1-y)}X''_{3y}$, in which Ln' and Ln" are two

different rare earths of the Ln type, X' and X" being two different halogens of the X type, especially Cl and Br, it being possible for x to range from 0 to 1 and for y to range from 0 to 1;

- $RbGd_2Br_7$, which may in particular be doped with 0.1 to 50 wt% $CeBr_3$;
- $RbLn_2Cl_7$, which may in particular be doped with 0.1 to 50 wt% $CeCl_3$;
- $RbLn_2Br_7$, which may in particular be doped with 0.1 to 50 wt% $CeBr_3$;
- $CsLn_2Cl_7$, which may in particular be doped with 0.1 to 50 wt% $CeCl_3$;
- $CsLn_2Br_7$, which may in particular be doped with 0.1 to 50 wt% $CeBr_3$;
- K_2LaCl_5, which may in particular be doped with 0.1 to 50 wt% $CeCl_3$;
- K_2LaI_5, which may in particular be doped with 0.1 to 50 wt% CeI_3; and
- LuI_3, which may in particular be doped with 0.1 to 50 wt% CeI_3.

The term "dopant" or the term "doped" refers to a rare earth present in a minor proportion) that substitutes for one or more rare earths present in a major proportion, the rare earths present in both minor and major proportions being included by the symbol Ln.

As preferred rare-earth halide, mention may be made of:

- $LaBr_3$ doped with 5 to 15 wt% $CeCl_3$; and
- $LaCl_3$ doped with 5 to 15 wt% $CeCl_3$.

The invention is not limited to the use of a Tl:NaI or lanthanum halide crystal as detector. Detectors giving good energy resolution (especially over a wide energy range) and/or a good response time (in particular less than 100 ns) may usefully be employed in combination with the LiF crystal according to the invention. Such crystals may for example be YAP (yttrium aluminum perovskite) especially Ce()-doped or YAG (yttrium

aluminum garnet) or Ge (germanium).

EXAMPLES

Single crystals of pure LiF or those doped with Mg in fluoride form were prepared from a uniform blend of pure LiF and pure MgF^2 powders in various concentrations. The blend was placed in a platinum crucible and then melted by heating to 950°C. A crystallization operation was then carried out, resulting in a single crystal 2 300 cm^3 in volume.

The reflected X-radiation intensity was measured on single-crystal pieces cleaved along the (200) plane, with the molybdenum K_α line. The intensity varied little within an Mg concentration range between 0 and 400 ppm by weight. The intensity from the highly magnesium-doped Mg:LiF single crystals was expressed as a percentage of the intensity from the specimen containing 300 ppm Mg by weight. These results are given in Table 1. In this table, the specimen name contains the Mg content.

Table 1

Specimen	Mg content (in ppm by weight)	Mg content (mol/kg)	% intensity relative to LiF_{300}
pure LiF	0	0	100%
LiF_{300}	300	0.0123	100%
LiF_{501}	501	0.0206	336%
LiF_{664}	664	0.0273	476%
LiF_{765}	765	0.0314	552%
LiF_{1063}	1063	0.0437	589%

The effect of wavelength on the reflected intensity was also measured on specimens having a different Mg content. Table 2 gives the results. These results are expressed as a percentage of the reflected intensity for LiF_{300}. The reflected intensity increases very

strongly when the wavelength decreases for specimens having a higher Mg content.

Table 2

	λ = 3.359 Å	λ = 2.750 Å	λ = 1.937 Å	λ = 1.542 Å	λ = 0.7107 Å
	Ca	Ti	Fe	Cu	Mo
LiF_{300}	100%	100%	100%	100%	100%
LiF_{765}	207%	252%	358%	410%	572%
LiF_{1063}	238%	285%	404%	441%	595%

The increase in intensity, measured with a cleaved surface finish (on a (200) crystallographic plane), is maintained after plane plates have been curved. For example, at the iron wavelength (λ = 1.937 Å), the intensity reflected by the cleaved plane LiF_{664} was 2.8 times higher than that of cleaved plane LiF_{300}. The intensity reflected by curved LiF_{664} plates, curved over a cylinder whose axis was parallel to the X-ray direction, remained higher than the intensity reflected by the curved LiF_{300} plates, again curved over the same cylinder with its axis parallel to the direction of the X-rays. The intensity ratio of the plates curved over a cylinder of axis parallel to the X-ray beam remained the same (i.e. 2.8).